

**OFFICE OF NAVAL RESEARCH**

FINAL REPORT

END OF THE YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENT REPORTS

for

**GRANT: N00014-92-J-1374**

**R&T CODE: 413x00**

**NEW THIOPHENE-BASED MATERIALS**

BY

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JULY 3, 1995

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OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413x00

Contract/Grant Number: N00014-92-J-1374

Contract/Grant Title: New Thiophene-Based Materials

Principal Investigator: Joseph M. DeSimone and Edward T. Samulski

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E-mail Address: DESIMONE@UNCVX1.OIT.UNC.EDU. and et@UNC.EDU.

- a. Number of papers submitted to refereed journals, but not published: 0
- b. \* Number of papers published in refereed journals (for each, provide a complete citation): 10
- c. Number of books or chapters submitted, but not yet published: 0
- d. \* Number of books or chapters published (for each, provide a complete citation): 1
- e. \* Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
- f. Number of patents filed: 1
- g. \* Number of patents granted (for each, provide a complete citation): 1
- h. \* Number of invited presentations (for each, provide a complete citation): 2/0
- i. \* Number of submitted presentations (for each, provide a complete citation): 3
- j. \* Honors/Awards/Prizes for contract/grant employees (list attached): 6  
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:  
Graduate Students: 2  
Post-Doctoral Associates: 1  
including the number of,  
Female Graduate Students: 1  
Female Post-Doctoral Associates: 0  
the number of  
Minority Graduate Students: 1  
Minority Post-Doctoral Associates: 0  
and, the number of  
Asian Graduate Students: 0  
Asian Post-Doctoral Associates: 0
- l. \* Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

\* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

## ONR END-OF-THE-YEAR REPORT

### PART I

A. Number of papers submitted to refereed journals, but not published:

B. Number of papers published in refereed journals:

1. "Isomeric poly(benzophenone)s: Synthesis of highly crystalline poly(4,4'-benzophenone) and amorphous poly(2,5-benzophenone), A soluble poly(p-phenylene) derivative", Phillips, R.W.; Sheares, V.V.; Samulski, E.T. and DeSimone, J.M. *Macromolecules*, **1994**, 27, 2354.

2. "Thiophene-based poly(arylene ether)s: 5. Imide-arylene ether statistical copolymers", Sheares, V.V.; DeSimone, J.M.; Hedrick, J.L.; Carter, K.R.; Labadie, J.W. *POLYMER*, 94/0146.

3. "Thiophene-based poly(arylene ether)s. 4. Synthesis of poly(arylene ether sulfone)s", Archibald, R.S.; Sheares, V.V.; Samulski, E.T.; and DeSimone, J.M. *Macromolecules*, **1993**, 26, 7083-7085.

4. "Electric dipole interactions of chain solutes in nematics: The analysis of segmental ordering in dibromoalkanes", D.J. Photinos and E.T. Samulski, *J. Chem. Phys.*, **1993**, 98, 10009-10016.

5. "Organic low molar mass and polymeric liquid crystalline NLO materials", H. Wang, M.Y. Jin, R.C. Jarnagin and E.T. Samulski, *SPIE Organic & Biological Otoelectronics Symposium Proc.*, **1993**, 1853, 89-98.

6. "Thiophene-based liquid crystalline poly(benzoxazole)s" J.H. Promislow, J. Preston, and E.T. Samulski, *Macromolecules*, **1993**, 26, 1793-1795.

7. "Cyclic versus Linear Siloxane Liquid Crystals: Phas Behavior and X0ray Diffraction Results" T.J. Bunning, H.E. Klei, E.T. Samulski, W.W. Adams and R.L. Crane, *Mol. Cryst. Liq. Cryst.*, **1993**, 231, 153-174.

8. "a-helical polypeptide materials", E.Enriquez, M.Y. Jin, R.C. Jarnagin and E.T. Samulski, *Materials Research Society Symp. Proc.* **1993**, 292, 163-168.

9. "Oblate hexaalkoxy triphenylene solutes in a prolate nematic sovlent: A deuterium NMR study of alkyl chain ordering" Z. Luz, D.J. Photinos, and E.T. Samulski, *JACS*, **1993**, 115, 10895-900.

10. "Liquid crystalline polyesters containing isophthalic acid" R. Cai and E.T. Samulski, *Macromolecules* 27, 135-42 (1994).

C. Number of books or chapters submitted, but not yet published:  
None

D. Number of books or chapters published: 1

"The Mesomorphic State" E.T. Samulski, Physical Properties of Polymers, 2nd Edition, 1993, Chap. 5, 201-262, ACS Professional Reference Book, Edt. J.E. Mark.

E. Number of printed technical report/non-refereed papers: 0

F. Number of patents filed: Thiophene containing poly(arylene ether)sulfone. U.S. 08-099,731. Filed 7/30/93.

G. Number of patents granted: 1

"Thiophene-based Polymers" E.T. Samulski, US Patent #5,266,677; Date of Patent, November 20, 1993.

H. Number of invited presentations:

Joseph M. DeSimone

1. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", Gordon Research Conference - Polymers, June 29, 1993.

2. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", W.R. Grace, July 15, 1993.

3. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide" Phillips Petroleum, July 26, 1993.

4. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", DuPont, August 15, 1993.

5. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", Dow Corning, August 18, 1993.

6. "Thiophene-based Poly(arylene ether ketone)s and Poly(arylene ether sulfone)s", Symposium on Polyethers, ACS PMSE Division, Chicago, August 22-27, 1993.

7. "Cationic Polymerizations in Supercritical Carbon Dioxide", ONR Workshop on Energetic Materials, Elkton, MD, September 10, 1993.

8. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide" Cambridge University, UK, September 13, 1993.
9. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide" University of Durham, UK, September 14, 1993.
10. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide" Keynote Lecturer for the Third Nottingham/Leeds Supercritical Chemistry Symposium in Nottingham, UK; September 16, 1993.
11. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide" POLYMEX-93-International Symposium on Polymers, Cancun, Mexico, November 1-5, 1993.
12. "Emulsion Polymerizations in Carbon Dioxide", American Institute of Chemical Engineering National Meeting, St. Louis, MO, November 10, 1993.
13. "Emulsion Polymerizations in Carbon Dioxide" Air Products, November 1, 1993.
14. "Emulsion Polymerizations in Carbon Dioxide" Pittsburgh ACS Polymer Group Meeting, Pittsburgh, PA, November 17, 1993.
15. "Emulsion Polymerizations in Carbon Dioxide" Duke University, November 19, 1993.
16. "Dispersion Polymerization in Carbon Dioxide", Atochem North American, November 24, 1993.
17. "Thermally Stable Engineering Polymers via Ni(o)-coupling of Bisarylchlorides", Virginia Tech, December 3, 1993.
18. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", W.L. Gore and Associates, December 10, 1993.
19. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", 3M, December 13, 1993.
20. "Homogeneous and Heterogeneous Polymerizations in Supercritical Carbon Dioxide", DuPont, December 22, 1993.

Edward T. Samulski

1. "Molecular Flexibility in LCs", Kent State Univ. (Kent OH); May 5, 1993.
2. "NLO Studies of Siloxane LCs" Wright-Patterson AFB (OH); May 6, 1993.

3. "New High Performance Polymers Based on Thiophene" Univ. Cincinnati, (OH), May 7, 1993.

4. "New High Performance Polymers based on Thiophene", Polymex 93 (Cancun, Mexico) November 4, 1993.

5. "Polybenzyl-L-glutamate is 50 years old?" Univ. Virginia (VA) February 28, 1994.

6. "Recent Advances in RheoNMR" Cornell Univ. (NY) March 1, 1994.

I. Number of submitted presentations:

J.M. DeSimone

1. "Flagellenes: Nanophase-separated, Polymer-substituted Fullerenes", Samulski, E.T.\*, DeSimone, J.M.; Hunt, Jr., M.O.; Menciloglu, Y.Z.; Jarnagin, R.C.; York, G.A.; Lablat, K.B.; Wang, H. *Polymer Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 1993, 34(1), 85.

2. "Thiophene-based Poly(arylene ether ketone)s and Poly(arylene ether sulfone)s" Sheares, V.V.; Archibald, S.A.; Samulski, E.T.; DeSimone, J.M.\*, *Polymer Prepr. (Am. Chem. Soc. Div. Polym. Mats. Sci. Eng.)*, 1993, 69,236.

3. "Thiophene-based poly(arylene ether sulfone)s: Polymerization of 2-Chloro-5-(4'-halophenylsulfonyl)thiophene with 4,4'-Isopropylidenediphenol" Archibald, S.A.; Sheares, V.V.; Samulski, E.T.; DeSimone, J.M.\*. *Polymer Prepr. (Am. Chem. Soc. Div. Polym. Mats. Sci. Eng.)*, 1993, 69,247.

J. Honors/Awards/Prizes for contract/grant employees:

J.M. DeSimone

1993 Philip and Ruth Hettleman Prize for Artistic and Scholarly Achievement.

1993-1997 Presidential Faculty Fellow Award.

1993 Unilever Exploratory Research Award.

E.T. Samulski

1994 Stone Award of the Carolina Piedmont Section of the ACS (Southeast Region).

1994 Cary C. Boshamer Professor of Chemistry (Endowed Chair).

1993 Chairman-elect 1995 Gordon Conference on Polymers.

K. Total number of Full-time equivalent Graduate students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students: 2 Valerie Sheares and Theo Dingemans

Post-doctoral: 1 Scott Archibald  
Including the number of female graduate students: 1  
Female Post-doctoral associates: 0  
The number of Minority Graduate Students: 1  
Minority Post-doctoral Associates: 0  
The number of Asian Graduate Students: 0  
Asian Post-doctoral associates: 0

L. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

J.M. DeSimone and E.T. Samulski

NSF, "Young Investigator Award", Funded for first year at \$62,500. [J.M. DeSimone] (Used to supplement laboratory in general).

Presidential Faculty Fellow Award, National Science Foundation, July, 1993 Funded 4 years for \$400,000. (Used to supplement laboratory in general).

"Polymer Synthesis in SCF's", Exxon Research and Engineering, October, 1993 Funded 1st year \$15,000.

"Materials Synthesis and Processing in Carbon Dioxide", NSF/EPA submitted to NSF/CCr call for proposals entitled "Environmentally Benign Chemical Synthesis and Processing" (w/K.P. Johnston - Department of Chemical Engineering, University of Texas at Austin) Funded 3 years for \$555,043. (Not related to ONR N00014-92-J-1374).

"Heterogeneous Polymerizations in SCFs (w/E.T. Samulski) (DuPont, Hoechst-Celanese, Air Products) Funded 3 years for \$500,000. (Not related to ONR N00014-92-J-1374).

DuPont, "Polymerizations in Supercritical Fluids" December, 1992, December, 1995 funded for first year at \$160,000. [J.M. DeSimone]. (Not related to ONR N00014-92-J-1374).

"Genetically Tailored Polypeptides", NC Biotech, June 1, 1993-Nov. 30, 1994 submitted Jan 1, 1993, \$40,000 [E.T. Samulski]. (Not related to ONR N00014-92-J-1374).

"Thiophene-based Materials Consortium", Hoechst-Celanese, July 1, 1992-June 30, 1995, submitted June, 1991 for \$147,000. (E.T. Samulski and J.M. DeSimone) (directly related to ONR N00014-92-J-1374).

"Thiophene-based Materials Consortium", DuPont, July 1, 1992-June 30, 1995, submitted June, 1991 for \$147,000. (E.T. Samulski and J.M. DeSimone) (Directly related to ONR N00014-92-J-1374).

"NLO Properties of Polypeptide Derivatives", USAF, April, 1991-March 1996, funded(\$676,000); yr-1 \$115k; yr-2 \$150k; yr-3 \$150k (E.T. Samulski and R.C. Jarnagin). (Not related to ONR N00014-92-J-1374).

"RheoNMR", Imperial Oil Canada, July 1, 1993-Dec. 31, 1994, submitted April 20, 1993, \$20,952 (w/Y. Wu). (Not related to ONR N00014-92-J-1374.)

"Clustering and Migration in Perfluoroalkyl-Terminated Polymers," HCC-UNC May 1, 1993-August 1, 1994, funded for one year for \$20,000. (Not related to ONR N00014-92-J-1374.)

## PART II

A. Principal Investigator: Joseph M. DeSimone and Edward T. Samulski

B. Phone: (919) 962-2166 [JMD]; (919) 962-1561 [ETS]

C. Cognizant ONR Officer: Dr. Kenneth J. Wynne

D. Brief Description of Project:

Our research is focused on the general synthesis and characterization of new classes of thermoplastic and thermosetting engineering polymers from thiophene-based monomers and recently discovered synthetic methodologies. The approaches involve detailed investigations of the synthesis of thiophene-based poly(aramide)s, aromatic and aliphatic poly(ester)s, poly(benzbisoxazole)s, poly(arylene ether ketone)s, poly(imide)s, poly(arylene)s and poly(arylene sulfide)s using inexpensive monomers synthesized from thiophene-2,5-diacid chloride (made in > 90% yield from adipic acid and thionyl chloride!) and halothiophene derivatives.

E. Significant Results During the Last Year:

Research has led to successful syntheses in several areas including poly(ester)s, poly(arylene ether sulfone)s, poly(imide arylene ether)s, and most recently poly(benzophenone)s. (1) Novel homo and copolymer analogues of poly(ethylene terephthalate) were prepared using conventional transesterification methods. Ethylene glycol was reacted with various diester monomers containing *p*-phenylene, *m*-phenylene, 2,5-thiophene, biphenylene, or naphthalene units. All of the polymers in the series were high molecular weight with comparable decomposition temperatures suggesting that the thermal stability of PET and its analogues was not diminished by the heterocyclic thiophene ring. (2) Poly(arylene ether sulfone)s based on various bisphenols including 4,4'-isopropylidenediphenol, 4,4'-hexafluoroisopropylidenediphenol, and hydroquinone were synthesized and scaled up for gas permeability studies in the Dept. of Chemical Eng. at NCSU. Initial poly(arylene ether ketone) results suggest that the sulfone derivatives will have interesting properties. (3) Imide arylene ether statistical copolymers were synthesized using new thiophene-containing diamines with oxydianiline and pyromellitic dianhydride (Kapton monomers). The copolymers displayed



good film forming properties and sufficiently lowered the glass transition temperature such that these materials may have useful auto-adhesion properties for microelectronics applications. (4) Our newest area of interest poly(benzophenone)s employed the coupling of inexpensive readily available monomers 4,4'-dichlorobenzophenone and 2,5-dichlorobenzophenone. The polymerization of 2,5-DCBP yielded a soluble derivative of poly(*p*-phenylene). The Ni(O) catalyzed polymerization is a facile and economically feasible synthetic route and opens the way to a low temperature, mild reaction for a large variety of thiophene-containing homo- and copolymers.

#### F. Brief Summary of Plans for Next Year:

(1) We will continue to establish the structure/property relationships for these new polymers. The bilateral asymmetry of the heterocycle in the chain will certainly influence melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, and gas permeability properties relative to conventional phenylene-based materials. (2) We will continue gas permeability analysis of poly(arylene ether sulfone)s at NCSU. (3) We will extend the poly(2,5-benzophenone) homopolymers to include copolymers with 1,3- and 1,4-dichlorobenzophenone and 2,5-dichlorothiophene. In addition to these copolymers, cross-linkable materials will be synthesized via 2,5-dichloro-4'-methylbenzophenone and opto-electronic materials will be synthesized via thiophene-containing silane derivatives.

### EXPLANATORY TEXT FOR PART III

**Concept:** The objective of our research is the synthesis of novel thiophene-based polymer analogues of known polymers and the evaluation of the new polymer properties in the bulk and solution states. We are modifying existing classes of phenylene-based polymers through incorporation of thiophene moieties, i.e., introducing the quasi-functionality (sulfur) and the unique molecular geometry of the aromatic 2,5-thiophene moiety into the polymer backbone: 2,5-thiophene interjects an angle of 148° into the backbone; this geometry is between 180° and 120° angles associated with the commonly utilized *p*-phenylene and *m*-phenylene units, respectively. The bilateral asymmetry of the heterocycle in the chain will certainly influence melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, etc. relative to conventional phenylene-based materials.

**Background:** The thiophene analogues of Kevlar and PBO have been synthesized using conventional polymerization methods by substituting 2,5-thiophenecarboxylic acid for terephthalic acid. In both cases, high molecular weight lyotropic liquid crystalline polymers were obtained demonstrating the viability of the 2,5-thiophene moiety as a mesogenic core. This work in liquid crystalline polymers was extended to poly(arylene ether ketone)s. In order to synthesize direct thiophene analogues of commercially important materials such as PEEK, we developed a new polymerization methodology involving the formation of phenyl-thienyl ether bonds in the polymer forming reaction. Our initial polymer was made from bis(5-chlorothiophenyl-2) ketone and bisphenol-A using standard polymerization reaction conditions (weak base, azeotroping solvent system) (40K g/mol by GPC). The versatility of this synthetic route, which uses phenyl-thienyl ether bond formation as a polymer-forming reaction, was

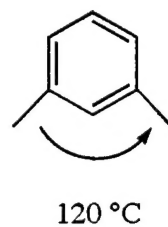
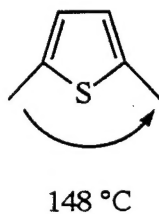
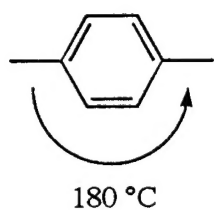
demonstrated in polymers synthesized from 5-(4-fluorobenzoyl)-2-chlorothiophene with bisphenol-A, bisphenol-AF, and 9,9'-HPF. The glass transition temperatures of the materials varied from 150 to 200°C. We anticipate that the introduction of the thiophene into these polymers in addition to the inherent properties of the bisphenols will play an important role in tailoring structure-property relationships, especially in gas permeability and permselectivity studies. Initial work in this area has been completed at NCSU and has been submitted for publication.

**Current Work:** Using the thiophene diacid chloride monomer, thiophene analogues of PET have been synthesized and showed comparable thermal stability to phenyl derivatives. Thiophene analogues of poly(arylene ether sulfone)s based on 2-fluoro-5-[(4'-chlorophenyl)sulfonyl]thiophene and bisphenol-A, bisphenol-AF or hydroquinone were high molecular weight indicative of the quantitative nature of the substitution chemistry utilized. These materials will be interesting analogues not only to phenyl-based systems, but also to the thiophene PAEKs in permeability studies. Imide aryl ether thiophene copolymers were prepared where the 2,5-thiophene moiety was incorporated via a meta or para diamine. The resulting polymers were film forming and showed tough ductile mechanical properties with high glass transition temperatures. Semicrystalline and amorphous poly(benzophenone)s have also been synthesized via Ni(O) catalyzed polymerizations of bisarylchlorides.

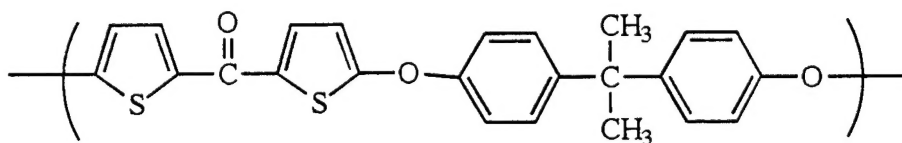
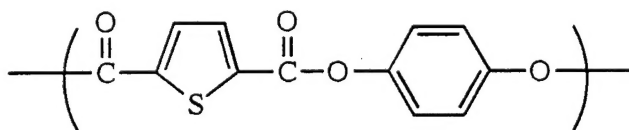
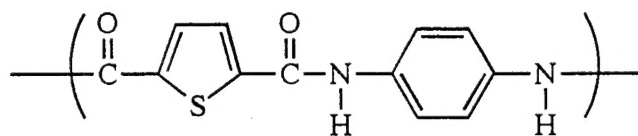
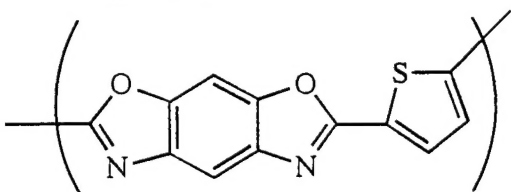
**New Systems:** The Ni(O) coupling chemistry is presently being extended to copolymers with *p*-dichlorobenzene, *m*-dichlorobenzene, and 2,5-dichlorothiophene. In addition, the methylated monomer will open the way to crosslinkable systems. The silane polymers based on thiophene are accessible via this chemistry and should exhibit unusual electro-optic characteristics.

## New Thiophene-Based Materials

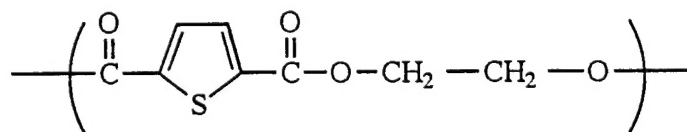
### Concept:



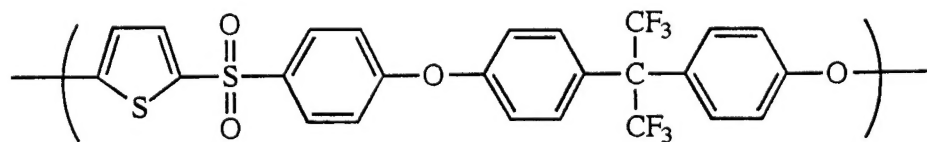
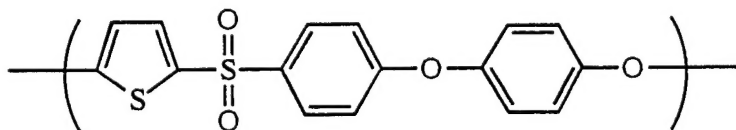
### Background:



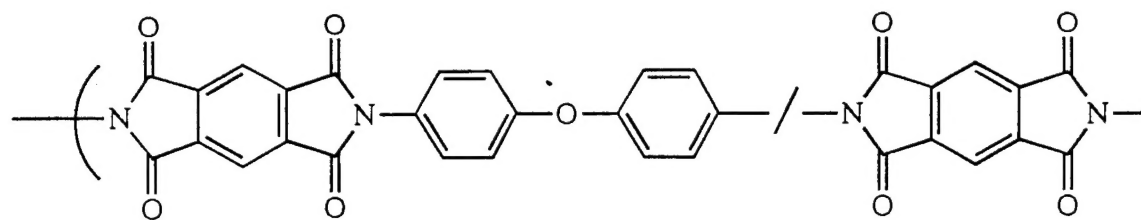
### Current Work: Poly(ester)s



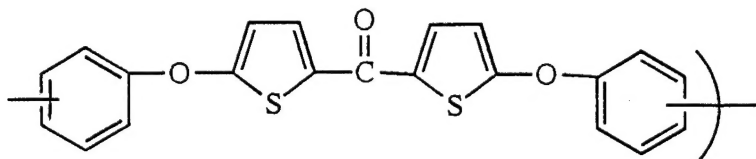
### Poly(arylene ether sulfone)s



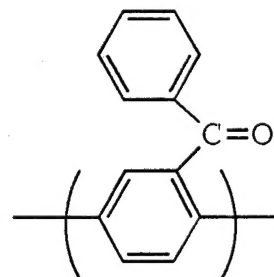
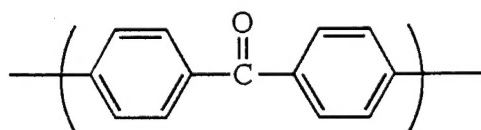
## Poly(arylene ether imide)s



3,3'- and 4,4'-



## Poly(benzophenone)s



## New Systems:

